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TITLE: CARBONACEOUS CRUCIBLE FOR PULLING UP SINGLE CRYSTAL AND ITS PRODUCTION
PUBN-DATE: September 12, 2000

INVENTOR-INFORMATION:

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NAME	COUNTRY
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APPL-NO: JP11055233
APPL-DATE: March 3, 1999

INT-CL (IPC): C30B015/10

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a carbonaceous crucible which is used for pulling up a single crystal and has excellent durability and a long use life by lowering the reactivity with a quartz crucible to control the generation of SiO gas and preventing the formation of SiC in the pores of the carbonaceous crucible due to the SiO gas, and to provide a method for producing the same.

SOLUTION: This carbonaceous crucible for pulling up the single crystal comprises a C/C(carbon fiber-reinforced carbon material) substrate-SiC composite product prepared by filling 35-50 vol.% of the total pore volume of the C/C substrate with the SiC deposited by CVI method. The method for producing the carbonaceous crucible comprises setting the C/C substrate to a CVI device, evacuating the CVI device up to 4 Torr, instantaneously charging a raw material gas containing a halogenated organic silicon compound in a concentration of 8-25 mol.% into the evacuated device at a temperature of 1,100-1,200

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TITLE: Carbonaceous crucible for supporting quartz crucible used for drawing single crystal, comprises base material filled with specific volume percent of silicon carbide and silicon carbide composite

PATENT-ASSIGNEE: TOKAI CARBON KK[TOJW]

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ABSTRACTED-PUB-NO: JP2000247779A

BASIC-ABSTRACT:

NOVELTY - Carbonaceous crucible comprises base material, 35-50 volume percent of the total blow volume of which is filled with silicon carbide precipitated by chemical vapor deposition and silicon carbide composite.

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for manufacture of carbonaceous crucible which involves baking, carbonizing a molded crucible (as base material) impregnated with resin matrix and hardened in a non-oxidizing atmosphere inside a CVI apparatus evacuated to 4 torr or less using mixed gas containing 8-25 mol.% of halogenated organosilicon and halogenated hydrogen. The apparatus is heated to 1100-1200 deg. C. Thermolysis of the mixed gas is carried out for predetermined time until silicon carbide precipitates. The process is repeated as a single pulse and precipitation filling of SiC is carried out in the blow hole of base material.

USE - For supporting quartz crucible used for drawing single crystal.

ADVANTAGE - The carbonaceous crucible is durable and has low reactivity with quartz crucible. Generation of silicon oxide gas is effectively restricted. Silicon carbonization is prevented.

CHOSEN- Dwg.0/0

DRAWING:

TITLE- CARBONACEOUS CRUCIBLE SUPPORT QUARTZ CRUCIBLE DRAW SINGLE CRYSTAL
TERMS: COMPRISE BASE MATERIAL FILLED SPECIFIC VOLUME SILICON CARBIDE
SILICON CARBIDE COMPOSITE

DERWENT-CLASS: E36 L03 U11

CPI-CODES: E31-P06C; L04-A01; L04-B01; L04-D09;

EPI-CODES: U11-B01;

CHEMICAL- Chemical Indexing M3 *01* Fragmentation Code B114 B720 B740 B831
CODES: C106 C800 C802 C803 C805 C806 C807 M411 M781 M904 M905 M910 Q454
R032 Specfic Compounds 01247K 01247U Registry Numbers 1247U

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(54)【発明の名称】 単結晶引き上げ用炭素質ルツボとその製造方法

(57)【要約】

【課題】 石英ルツボとの反応性を低下させてSiOガスの発生を抑止し、SiOガスによる炭素質ルツボ気孔内のSiC化を防止することにより耐久性に優れ使用寿命の長い単結晶引き上げ用炭素質ルツボとその製造方法を提供する。

【解決手段】 C/C基材の全気孔容積の35～50 vol%がCVI法により析出したSiCで充填されたC/C材とSiCの複合体からなる単結晶引き上げ用炭素質ルツボ。その製造方法はC/C基材をCVI装置にセットして4Torr以下に真空排気し、1100～1200℃の温度で原料ガス中のハロゲン化有機珪素化合物の濃度を8～25 mol%に設定して瞬間導入し、所定時間保持する、という一連の操作を1パルスとして所定回数繰り返し行い、C/C基材の気孔内にSiCを析出充填する。

【特許請求の範囲】

【請求項1】 炭素繊維強化炭素材を基材とし、該基材の全気孔容積の35～50 vol%がCVI法により析出したSiCで充填された炭素繊維強化炭素材とSiCの複合体からなることを特徴とする単結晶引き上げ用炭素質ルツボ。

【請求項2】 炭素繊維にマトリックス樹脂を含浸、硬化したルツボ成形体を非酸化性雰囲気下に焼成炭化して得られた炭素繊維強化炭素材を基材とし、該基材をCVI装置にセットして、系内を4Torr以下の圧力に真空排気する工程、1100～1200℃の温度に加熱しながらハロゲン化有機珪素化合物と水素との混合ガスを原料ガスとして原料ガス中のハロゲン化有機珪素化合物の濃度を8～25 mol%に設定して瞬間導入する工程、原料ガスをCVI反応により熱分解してSiCを析出させるために所定時間保持する工程、とからなる一連の操作を1パルスとして繰り返し行い、基材の気孔内にSiCを析出充填することを特徴とする請求項1記載の単結晶引き上げ用炭素質ルツボの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、チョコラルスキー法（以下「CZ法」という）によるシリコンなどの単結晶引き上げ装置に使用される石英ルツボを支持するために用いる炭素質ルツボに関する。

【0002】

【従来の技術】ICやLSIなどの製造に用いるシリコンなどの単結晶は、通常CZ法により製造されている。CZ法は、高純度の石英ルツボの中にシリコン多結晶を入れ、石英ルツボを所定速度で回転させながらヒータによりシリコン多結晶を加熱溶解し、シリコン多結晶の溶解液の表面に種結晶（シリコン単結晶）を接触させて、所定速度で回転させながらゆっくりと引上げることによりシリコン多結晶の溶解液を凝固させて、シリコン単結晶に成長させるものである。

【0003】しかしながら、石英ルツボは高温においては軟化し、強度も充分でないので、通常、石英ルツボは炭素ルツボ内に嵌合され炭素ルツボで石英ルツボを支持することにより補強して用いられている。この石英ルツボを嵌合する炭素ルツボとしては高温強度が高く、耐熱性や熱伝導率が高い黒鉛材が一般的に使用されている。しかしながら、黒鉛材は表面から黒鉛の微粉が離脱、飛散し易いので装置内を浮遊してシリコン溶解液中に混入し、シリコン単結晶の品質を低下させる難点がある。

【0004】また、材質上石英と黒鉛とは熱膨張係数が大きく異なるために、加熱、冷却を繰り返し行っている間に加熱時には石英ルツボが軟化して黒鉛ルツボに密着し、一方冷却時には黒鉛ルツボの収縮量が石英ルツボの収縮量に比べて大きくなることにより石英ルツボから内

圧を受けることとなり、黒鉛ルツボの変形、割損などが生じる難点もある。

【0005】更に、高温加熱時に石英ルツボ（SiO₂）と黒鉛ルツボ（C）とは接触する嵌合面において反応してSiOガスを発生し、発生したSiOガスは黒鉛ルツボ表層部の気孔内に浸透しながら黒鉛ルツボ（C）と反応して黒鉛ルツボの表層部の気孔内から次第に内部にまでSiCに転化する。したがって、このような加熱処理が繰り返されると、黒鉛ルツボ内における黒鉛とSiCとの材質性状、例えば熱膨張係数の相違によりマイクロクラックが発生して、遂には黒鉛ルツボの割損を招くこととなる。

【0006】この難点を解決するために、特開昭63-166789号公報には、少なくとも黒鉛の気孔の内部表面を有機珪素高分子化合物であるポリカルボシランを原料とする炭化珪素膜で被覆してなるシリコン単結晶引上装置用黒鉛製ルツボ、及びポリカルボシランを少なくとも黒鉛の気孔の内部に含浸充填した後、酸性雰囲気中の50～400℃下で不融化させ、さらに不活性雰囲気中の1000～2000℃下で焼成し前記ポリカルボシランを熱分解して形成するシリコン単結晶引上装置用黒鉛製ルツボの製造方法が提案されている。

【0007】この特開昭63-166789号公報の技術によれば、石英ルツボを嵌合する黒鉛ルツボの内部表面の気孔内をSiCに転化して、石英ルツボと黒鉛ルツボの反応を抑止することによりSiOガスの発生を抑制し、またSiOガスとの反応による黒鉛ルツボ内部表面のSiC化を防止するものである。しかしながら、有機珪素高分子化合物であるポリカルボシランの含浸充填は、アセトンやヘキサンなどの有機溶媒にポリカルボシランを溶解した溶液中に黒鉛素材を浸漬するなどの方法により行われるので、黒鉛素材の表面部に存在する、例えば数十ミクロン以下の微細な気孔中に充填することは極めて困難である。

【0008】そこで、黒鉛に比べて強度特性に優れ、また石英との熱膨張係数の差異が少ない炭素繊維強化炭素材（以下「C/C材」ともいう）を用いて炭素ルツボを構成する提案も行われており、例えば、少なくとも側壁部分が一体のC/C材により構成されてなる単結晶引き上げ用ルツボ（実開昭63-7174号公報）、ルツボ内側を炭素繊維クロス積層体または炭素繊維フェルト積層体を用いたC/C材とし、ルツボ外側をフィラメントワインディング法により成形したC/C材で構成した二層よりなるシリコン単結晶引き上げ用炭素繊維強化炭素ルツボ（特開平9-263482号公報）、などが提案されている。

【0009】

【発明が解決しようとする課題】しかしながら、これらのC/C材からなる炭素ルツボであっても、上記した石英ルツボとの反応によるSiOガスの発生や発生したSiOガスが炭素ルツボ表層部の気孔内部に拡散し気孔内

面と反応してSiCへ転化させる現象を防止することはできないという問題点がある。

【0010】そこで、本発明者は、黒鉛材に比べて強度特性に優れたC/C材を対象として耐久性に優れた炭素質ルツボの開発について鋭意研究を進めた結果、化学的気相充填法によりSiCを析出させることによりC/C材の表層部に存在する微細な気孔内部にまでSiCを充填させることが可能であり、更にその炭素質ルツボを用いて、多数回の単結晶引き上げ操作を繰り返し安定に行うことのできることを見出した。

【0011】本発明は、この知見に基づいて完成したものであり、その目的は石英ルツボとの反応性が抑制されてSiOガスの発生を抑止し、また発生したSiOガスが炭素質ルツボ表層部の気孔内部に拡散し気孔内面と反応してSiCに転化する現象が抑止されることにより、多数回の引き上げ操作を安定に繰り返し行うことが可能な単結晶引き上げ用炭素質ルツボとその製造方法を提供することにある。

【0012】

【課題を解決するための手段】上記の目的を達成するための本発明の単結晶引き上げ用炭素質ルツボは、炭素繊維強化炭素材を基材とし、該基材の全気孔容積の35～50 vol%がCVI法により析出したSiCで充填された炭素繊維強化炭素材とSiCの複合体からなることを構成上の特徴とする。

【0013】また、その製造方法は、炭素繊維にマトリックス樹脂を含浸、硬化したルツボ成形体を非酸化性雰囲気下に焼成炭化して得られた炭素繊維強化炭素材を基材とし、該基材をCVI装置にセットして、系内を4 Torr以下の圧力に真空排気する工程、1100～1200℃の温度に加熱しながらハロゲン化有機珪素化合物と水素との混合ガスを原料ガスとして原料ガス中のハロゲン化有機珪素化合物の濃度を8～25 mol%に設定して瞬間導入する工程、原料ガスをCVI反応により熱分解してSiCを析出させるために所定時間保持する工程、とからなる一連の操作を1パルスとして繰り返し行い、基材の気孔内にSiCを析出充填することを構成上の特徴とする。

【0014】

【発明の実施の形態】本発明の単結晶引き上げ用炭素質ルツボは、ポリアクリロニトリル系、レーヨン系、ビッチ系などの各種原料から製造された炭素繊維を強化材として、これらの炭素繊維がフェノール系やフラン系などの熱硬化性樹脂を焼成炭化した炭化物により結着され、一体化されたC/C材を基材として、このC/C基材の全気孔容積の35～50 vol%がCVI法により析出したSiCにより充填されたC/C材とSiCの複合体の組織構造から構成された点に特徴がある。

【0015】C/C材には種々の大きさの気孔が存在しており、C/C材を用いてCZ法による単結晶引き上げ

用の炭素質ルツボを作製した場合には、高温加熱時に嵌合する石英ルツボとの接触面において石英ルツボと反応してSiOガスを発生し、生成したSiOガスがこの気孔内を速やかに浸透して、C/C材の気孔内面が容易にSiCに転化される。その結果、炭素質ルツボの気孔内が次第にSiC化していき、その結果ミクロクラックが発生し易く、強度特性に優れたC/C材であっても割損することとなる。

【0016】そこで、本発明の炭素質ルツボは、C/C基材に存在する全気孔容積のうち、その35～50 vol%をCVI法（Chemical Vapor Infiltration；化学的気相浸透法）により析出沈着させたSiCにより充填したC/C材を用いて、すなわち炭素質ルツボをC/C材とSiCとの複合体から構成することにより、SiOガスの発生及び気孔内へのSiOガスの浸透によるSiC化を効果的に阻止するものである。

【0017】この場合、SiCの充填量として全気孔容積の35～50 vol%の範囲に設定するのは、充填量が35 vol%未満では石英ルツボとの反応によるSiOガスの発生ならびにSiOガスの気孔内への浸透によるSiC化の阻止効果が充分でないためである。しかしながら、50 vol%を超えてSiCを充填しても、CVI法によるSiCを析出沈着させる作業の煩雑さに比べてSiOガスの発生及び気孔内のSiC化を阻止する効果が小さくなるためである。

【0018】本発明の単結晶引き上げ用炭素質ルツボは下記の方法により製造される。まず、常法により炭素繊維織布をマトリックス樹脂液に浸漬またはマトリックス樹脂液を塗布するなどの方法で炭素繊維にマトリックス樹脂を含浸し、半硬化したプリプレグを所望のルツボ形状に成形し、硬化した成形体を非酸化性雰囲気中に保持された加熱炉中で焼成炭化することによりC/C材からなるルツボ成形体を作製する。なお、マトリックス樹脂としてはフェノール樹脂、フラン樹脂などの高炭化性の熱硬化性樹脂が用いられる。

【0019】あるいは、連続炭素繊維にマトリックス樹脂液を含浸し、フィラメントワインディング法によりルツボ形状に成形した成形体を硬化したのち、非酸化性雰囲気中に保持された加熱炉中で焼成炭化することによりC/C材からなるルツボ成形体を作製することもできる。

【0020】このようにして作製したC/C材からなるルツボ成形体をCVI装置にセットして、特定のCVI反応条件で処理することにより本発明の全気孔容積の35～50 vol%が気相析出して気孔内に沈着したSiCにより充填されたC/C材とSiCとの複合組織からなる炭素質ルツボが製造される。

【0021】CVI法（Chemical Vapor Infiltration）は、CVD法（Chemical Vapor Deposition）と異なり、微細な気孔または空隙内のミクロ表面へ気相蒸着することができる。CVI法はその手法によって、(a)均熱・

定圧型CVI、(b)強制流動CVI、(c)パルスCVI、などに大別される。このうち、パルスCVI法は、①反応系を真空排気して細孔中のガスの除去、②反応系への原料ガスの瞬間導入、③反応析出のための所定時間保持、を1パルスとして数千から数十万回繰り返すことにより比較的短時間で気孔深部まで析出物を充填することを可能とするものであり、本発明の目的にはパルスCVI法が好ましく適用される。但し、パルスCVI法に限定されるものではない。

【0022】C/C材からなるルツボ成形体は、CVI反応装置の基材受台に載置して加熱し、供給した原料ガスを気相熱分解してSiCを析出沈着させることにより、ルツボ成形体の気孔内を充填する。原料ガスには1分子中にSi原子とC原子とを含むメチルトリクロロシラン(CH_3SiCl_3)、メチルジクロロシラン($\text{CH}_3\text{SiHCl}_2$)などのハロゲン化有機珪素化合物と水素との混合ガスが用いられる。

【0023】CVI法により原料ガスを気孔内に浸透させて気相熱分解し、気孔内にSiCを析出充填させるためにはCVI反応条件を次のように設定制御する。①反応系内を真空排気して4Torr以下の減圧下に維持して、C/C基材の気孔内に存在するガスを排出除去する。減圧度が4Torrを超えると脱ガスの効果が不充分となり、気孔内深部に存在するガスを十分に排出除去できないために結果的に気孔深部にまでSiCを析出充填することが困難となる(真空排気工程)。

【0024】②反応系内を1100~1200℃の温度に加熱しながら、ハロゲン化有機珪素化合物と水素との混合ガスを原料ガスとして瞬間的に導入する。この場合、加熱温度が1100℃未満であると析出したSiC中に非晶質Siの遊離頻度が高くなり、また1200℃を超えると気孔内部、特に気孔深部へ充填することが難しくなる。更に、原料ガス中のハロゲン化有機珪素化合物の濃度を8~25 mol%の範囲に設定する。ハロゲン化有機珪素化合物の濃度が8 mol%未満であるとC/C基材の気孔内部への原料ガスの拡散に比べて原料ガスへの伝熱が速くなるためC/C基材表面への析出が優先する結果、気孔内部へのSiC充填が困難となる。しかしながら、濃度が25 mol%を超えると、気孔内部への原料ガス拡散に比較してC/C基材表面での反応頻度が高くなって基材面へのSiC析出が優先する結果、C/C基材の気孔内部へのSiC充填が困難となる(原料ガス瞬間導入工程)。この場合、気孔内部への最大充填量は35 vol%未満である。

【0025】③上記②で設定したCVI反応条件に所定時間保持することにより、気孔内部に所定量のSiCを析出充填する(保持工程)。

【0026】この①真空排気工程、②原料ガス瞬間導入工程、③保持工程、という一連の工程を1パルスとして、数千から数十万回繰り返すことによりC/C基材の

気孔深部にまでSiCを析出沈着させることができ、全気孔容積の35~50 vol%の気孔内を充填することが可能となる。このようにして、炭素質ルツボを構成するC/C基材の気孔内部及び表層面は高強度で耐酸化性に優れたSiCで充填、被覆され、シリコン単結晶引き上げ時の高温加熱時にも、石英ルツボとの反応性が低下し、SiOガスの発生及びC/C基材の気孔内部への浸透は効果的に抑止される。

【0027】以下、本発明の実施例を比較例と対比して具体的に説明する。

【0028】実施例1~3、比較例1~5

ポリアクリロニトリル系炭素繊維の二次元織クロスにフェノール樹脂初期縮合物を塗布して含浸し、風乾して作成したプリプレグシートを積層してモールドに入れ、250℃の温度に加熱して樹脂成分を硬化した。次いで、窒素ガス雰囲気中に保持した加熱炉中で10℃/hrの昇温速度により2000℃に加熱し、5時間保持して焼成炭化した。このようにして、25×25×4mmのC/C基材(Vf:約60%)からなるテストピースを作製した。

【0029】このテストピースを外熱式横型パルスCVI装置の反応炉内にセットし、系内を真空排気して炉内を3~4Torrに減圧した。次いで、加熱して所定温度に達したのち、トリクロロメチルシラン(CH_3SiCl_3)と水素との混合ガスを原料ガスとして炉内に導入し、所定の時間反応させて、CVI反応によりテストピースの気孔内にSiCを析出、充填した。この真空排気工程、原料ガス瞬間導入工程、保持工程、の一連の操作を1パルスとして繰り返しCVI反応を行い、SiCの析出、充填による重量増加率が25wt%前後になるまで繰り返し行った。この際、反応温度、原料ガス中のトリクロロメチルシラン濃度、パルス回数、などのCVI反応条件を変更した。なお、その他のCVI反応条件は下記のとおりである。

真空排気工程：排気時間；1.9秒

原料ガス導入工程：導入圧；200Torr、導入時間；0.7秒

保持工程：保持時間；1.0秒

1パルス；3.6秒

【0030】このようにしてテストピースにSiCを析出、充填したCVI反応条件を対比して表1に示した。

【0031】

【表1】

例No.	反応温度 (℃)	原料濃度 (mol%) *1	パルス回数
実施例1	1200	12.6	2000
実施例2	1100	10.0	4000
実施例3	1200	19.5	2000
比較例1	900	10.0	16000
比較例2	1000	10.5	9000
比較例3	1200	1.0	20000
比較例4	1200	26.3	2000
比較例5	1300	10.2	3000

(注) *1 トリクロロメチルシラン(CH_3SiCl_3)と水素とを混合した原料ガス中のトリクロロメチルシランの濃度【0032】比較例6

キシレンにポリカルボシランを20重量%の濃度に溶解した溶液中にテストピースを浸漬してポリカルボシランを含浸し、乾燥してキシレンを除去したのち、大気中250℃の温度に5時間加熱して不融化处理した。この処理を3回繰り返した後、窒素ガス雰囲気中で1500℃の温度に加熱してポリカルボシランを熱分解し、テストピースにSiC被膜を形成した。

【0033】次に、これらのSiCを析出、充填したテストピースについて、下記の方法により重量増加率、表面膜厚、充填率、表面膜質などを測定し、また耐酸化性試験を行った。得られた結果を表2に示した。

【0034】(1) 重量増加率；反応前後のテストピースの重量変化量を電子天秤で測定し、重量変化量を反応前のテストピースの重量で除して算出した。

(2) 表面膜厚；反応後のテストピースを切断し、切断面*

*を走査型電子顕微鏡で観察して膜厚を計測して、平均した。

(3) 充填率；反応後の体積増加分($\Delta w/\rho$) cm^3 からテストピースの表面析出体積($h S_0$) cm^3 を減じて得られる内部析出体積が、テストピースの細孔容積(V_p) cm^3/g に占める割合を充填率として、次式より算出した。

$$\text{充填率}(\text{vol}\%) = [(\Delta w/\rho) - (h S_0)] / (w_0 V_p) \times 100$$

10 但し、 Δw ；重量増加量、 h ；走査型電子顕微鏡写真から計測したテストピース表面の析出物膜厚、 w_0 ；テストピースの重量、 S_0 ；テストピースの表面積 ρ ；SiCの密度($3.10\text{g}/\text{cm}^3$)、 V_p ； $0.1452(\text{cm}^3/\text{g})$ である。

(4) 表面膜質；X線回折によってテストピース表面の結晶強度を評価した。

(5) 耐酸化性試験；大気雰囲気中の電気炉に入れて加熱し、500℃の温度に30分間保持したのち炉から取り出し常温まで自然冷却した。次に600℃の温度に加熱して30分間保持したのち炉から取り出し常温まで自然冷却した。このように100℃ずつ昇温して加熱する操作を1000℃まで行い、その時の重量減少率を下記式から算出して、耐酸化性を評価した。

$$\text{重量減少率}(\%) = (W_0 - W_{1000}) / (W_0) \times 100$$

但し、 W_0 は耐酸化試験前のテストピースの重量、 W_{1000} は1000℃まで加熱試験を行った後のテストピースの重量

【0035】

30 【表2】

例No.	重量増加率 (wt%)	表面膜厚 (μm)	充填率 (vol%)	表面膜質	重量減少率 (wt%)
実施例1	26.0	35	45	β -SiC	13.5
実施例2	27.4	35	46	β -SiC	16.1
実施例3	26.3	56	37	β -SiC	16.7
比較例1	24.0	26	44	非晶質Si	14.6
比較例2	26.8	34	47	非晶質Si	15.3
比較例3	23.3	88	20	β -SiC	19.3
比較例4	25.3	94	24	β -SiC	18.7
比較例5	22.7	126	9	β -SiC	21.4
比較例6	25.9	108	20	β -SiC	19.2

【0036】表1、2の結果から、実施例ではCVI法 ※充填されており、酸化処理による重量減少率が低位であ
で析出したSiCにより気孔容積の35～50vol%が※50 ることが認められる。一方、比較例1、2でも実施例1

〜3と同等の耐酸化性を示しているが、表面に形成された膜は非晶質Siであるため酸化処理によりSiO₂に転化して重量の増大を招き、重量減少率が見掛け上低位にあるものと判断される。更に、CVI温度が低いのでパルス回数を大幅に増やす必要があり、非効率となる。比較例3では原料濃度が低いためにパルス回数を多くしてもSiCの充填率が低く、酸化試験による減少率が大10 きいことが判る。比較例4では原料濃度が高いために基材面での膜厚が厚くクラックが発生し、そのうえSiCの充填率も低いために酸化試験による減少率が大

きいことが判る。

【0037】

【発明の効果】以上のとおり、本発明の単結晶引き上げ用炭素質ルツボは、C/C基材の全気孔容積の35〜50 vol%をCVI法により析出したSiCで充填したC/C材とSiCの複合体から構成されているので石英ルツボとの反応性が低く、SiOの発生が効果的に抑止されるのでSiOガスによる炭素質ルツボのSiC化が抑制され、使用寿命が長く、耐久性に優れた炭素質ルツボが提供される。また、その製造方法によれば、CVI反応条件を特定することにより耐久性に優れた炭素質ルツボを容易に製造することが可能となる。

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(54) CARBONACEOUS CRUCIBLE FOR PULLING UP SINGLE CRYSTAL AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a carbonaceous crucible which is used for pulling up a single crystal and has excellent durability and a long use life by lowering the reactivity with a quartz crucible to control the generation of SiO gas and preventing the formation of SiC in the pores of the carbonaceous crucible due to the SiO gas, and to provide a method for producing the same.

SOLUTION: This carbonaceous crucible for pulling up the single crystal comprises a C/C(carbon fiber-reinforced carbon material) substrate-SiC composite product prepared by filling 35-50 vol.% of the total pore volume of the C/C substrate with the SiC deposited by CVI method. The method for producing the carbonaceous crucible comprises setting the C/C substrate to a CVI device, evacuating the CVI device up to 4 Torr, instantaneously charging a raw material gas containing a halogenated organic silicon compound in a concentration of 8-25 mol.% into the evacuated device at a temperature of 1,100-1,200° C, retaining the charged state for a prescribed time, and repeating a series of the operations as one pulse prescribed times to deposit and fill the produced SiC in the pores of the C/C substrate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the carbonaceous crucible used in order to support the quartz crucible used for crystal pulling equipments, such as silicon by the Czochralski process (henceforth a "CZ process").

[0002]

[Description of the Prior Art] Single crystals, such as silicon used for manufacture of IC, LSI, etc., are usually manufactured by the CZ process. Putting in silicon polycrystal into the quartz crucible of a high grade, carrying out heating fusion of the silicon polycrystal at a heater, rotating a quartz crucible at predetermined speed, contacting seed crystal (silicon single crystal) on the front face of the melting liquid of silicon polycrystal, and making it rotate at predetermined speed, by pulling up slowly, a CZ process makes the melting liquid of silicon polycrystal solidify, and is grown up into a silicon single crystal.

[0003] However, since a quartz crucible is softened in an elevated temperature and reinforcement is not enough, either, the quartz crucible is usually reinforced and used by fitting in in a carbon crucible and supporting a quartz crucible by the carbon crucible. As a carbon crucible which fits in this quartz crucible, high temperature strength is high, and, generally graphite material with large thermal resistance and thermal conductivity is used. However, since the fines of a graphite break away and tend to disperse from a front face, graphite material floats, mixes the inside of equipment into silicon melting liquid, and it has the difficulty of reducing the quality of a silicon single crystal.

[0004] Moreover, there is also a difficulty which will receive a quartz crucible to internal pressure when a quartz crucible softens at the time of heating while a repeat line requires heating and cooling, since a construction material up quartz and a graphite have a large coefficient of thermal expansion and it differs, and it sticks to a graphite crucible and the amount of contraction of a graphite crucible becomes large [on the other hand / time / of cooling / the amount of contraction of a quartz crucible], and deformation of a graphite crucible, crack damage, etc. produce.

[0005] Furthermore, a quartz crucible (SiO_2) and a graphite crucible (C) react in the fitting side which contacts at the time of heating at high temperature, SiO gas is generated, and permeating in the pore of the graphite crucible surface section, the SiO gas which occurred reacts with a graphite crucible (C), and is gradually converted even into the interior out of the pore of the surface section of a graphite crucible at SiC . therefore, the construction material of the graphite in a graphite crucible if such heat-treatment is performed repeatedly, and SiC -- a micro crack will occur according to a difference of description, for example, a coefficient of thermal expansion, and crack damage of ***** will be caused at last.

[0006] In order to solve this difficulty, it is in JP,63-166789,A, The crucible made from a graphite for silicon single crystal raising equipments which comes to cover the polycarbosilane which is an organic silicon high molecular compound about the inner surface of the pore of a graphite at least with the silicon carbide film used as raw material, And after carrying out impregnation restoration of the polycarbosilane inside the pore of a graphite at least, Non-deliquesce is carried out under 50 in an acid ambient atmosphere - 400 **, it calcinates under 1000-2000 degrees C in an inert atmosphere further, and the manufacture method of the crucible made from a graphite for silicon single crystal raising equipments which pyrolyzes and forms said polycarbosilane is proposed.

[0007] According to the technology of this JP,63-166789,A, the inside of the pore of the inner surface of the graphite crucible which fits in a quartz crucible is converted into SiC , and generating of SiO gas is controlled by inhibiting the reaction of a quartz crucible and a graphite crucible, and SiC -ization of the graphite crucible inner surface by the reaction with SiO gas is prevented. However, since impregnation restoration of the polycarbosilane which is an organic silicon high molecular compound is performed by the method of a graphite raw material being immersed into the solution which dissolved polycarbosilane in organic solvents, such as an acetone and a hexane,

it exists in the surface section of a graphite raw material, for example, it is very difficult to be filled up into detailed pore dozens of microns or less.

[0008] Then, the proposal whose difference in a coefficient of thermal expansion with a quartz excel in a strength property compared with a graphite, and constitutes a carbon crucible using little carbon fiber consolidation carbon material (henceforth "C / C material") is also performed. For example, at least, the crucible for single crystal raising (JP,63-7174,U) and the crucible inside which the C/C material of one comes to consist of side-attachment-wall portions are made into the C/C material using a carbon fiber crossing layered product or a carbon fiber felt layered product, and the carbon fiber consolidation carbon crucible for silicon single crystal raising (JP,9-263482,A) which consists of a bilayer constituted from C/C material which fabricated the crucible outside with the filament winding method is proposed.

[0009]

[Problem(s) to be Solved by the Invention] However, there is a trouble that the phenomenon which generating of SiO gas and the SiO gas which occurred by the reaction with the above-mentioned quartz crucible are spread inside the pore of the carbon crucible surface section, reacts with a pore inner surface, and is made to convert to SiC cannot be prevented even if it is the carbon crucible which consists of these C/C material.

[0010] Then, the result of having advanced research wholeheartedly about development of the carbonaceous crucible which was excellent in endurance for the C/C material this invention person excelled [material] in the strength property compared with graphite material, By depositing SiC by the chemical gaseous-phase filling-up method, it is possible to make even the interior of the detailed pore which exists in the surface section of C/C material fill up with SiC, and it found out further that many single crystal raising actuation could be carried out to repeat stability using the carbonaceous crucible.

[0011] It is in offering the carbonaceous crucible for single crystal raising which many raising actuation is repeated to stability and can perform it, and its manufacture method by being inhibited the phenomenon which reactivity with a quartz crucible is controlled, that object inhibits generating of SiO gas, and the SiO gas which occurred is spread inside the pore of the carbonaceous crucible surface section, reacts [this invention is completed based on this knowledge,] with a pore inner surface, and converts into SiC.

[0012]

[Means for Solving the Problem] a carbonaceous crucible for single crystal raising of this invention for attaining the above-mentioned object -- carbon fiber consolidation carbon material -- a base material -- carrying out -- 35 - 50 vol% of total pore capacity of this base material -- CVI -- it is characterized by consisting of complex of carbon fiber consolidation carbon material filled up with SiC which deposited by law, and SiC on a configuration.

[0013] Moreover, the manufacture method uses carbon fiber consolidation carbon material obtained by carrying out matrix resin at impregnation and carrying out the baking carbonization of the hardened crucible Plastic solid under a non-oxidizing atmosphere at a carbon fiber as a base material, and sets this base material in CVI equipment. A process which sets concentration of a halogenation organosilicon compound in material gas as 8 - 25 mol%, and carries out flash installation by making mixed gas of a halogenation organosilicon compound and hydrogen into material gas while heating the inside of a system to a process and temperature of 1100-1200 degrees C which carry out evacuation to a pressure of 4 or less Torrs, Carrying out deposit restoration of the SiC into a repeat deed and pore of a base material is characterized by a series of actuation which consists of a process which carries out predetermined time maintenance in order to pyrolyze material gas by the CVI reaction and to deposit SiC on a configuration as one pulse.

[0014]

[Embodiment of the Invention] The carbonaceous crucible for single crystal raising of this invention makes reinforcement the carbon fiber manufactured from various raw materials, such as a polyacrylonitrile system, a rayon system, and a pitch system. It is bound with the carbide with which these carbon fibers carried out the baking carbonization of the thermosetting resin, such as a phenol system and a furan system, and the unified C/C material is used as a base material. 35 - 50 vol% of the total pore capacity of this C/C base material -- CVI -- the feature is that it consisted of organization of the complex of C / C material with which SiC which deposited by law was filled up, and SiC.

[0015] When the pore of various magnitude exists in C/C material and the carbon crucible for single crystal raising by the CZ process is produced using C/C material, in the contact surface with the quartz crucible which fits in at the time of heating at high temperature, it reacts with a quartz crucible, the SiO gas which generated and generated SiO gas permeates the inside of this pore promptly, and the pore inner surface section of C/C material is easily converted into SiC. Consequently, gradually, even if the inside of the pore of a carbon crucible is C / C material which turns, was easy to generate a micro crack as a result, and was excellent in the strength property SiC, it will be damaged by cracking.

[0016] Then, the inside of the total pore capacity to which the carbonaceous crucible of this invention exists in a

C/C base material, the 35 - 50 vol% -- CVI -- law (Chemical Vapor Infiltration; chemical gaseous-phase penetration method) The C/C material with which it was filled up by SiC which carried out deposit deposition is used. That is, by constituting a carbonaceous crucible from complex of C/C material and SiC, SiC-ization by generating of SiO gas and osmosis of the SiO gas into pore is prevented effectively.

[0017] In this case, because less than [35 vol%] is not enough as the inhibition effect of SiC-izing by generating of SiO gas according [a fill] to a reaction with a quartz crucible, and osmosis into the pore of SiO gas, it is set as the range of 35 - 50 vol% of total pore capacity as a fill of SiC. however -- even if filled up with SiC exceeding 50 vol% -- CVI -- it is because the effect which prevents generating of SiO gas and SiC-ization in pore compared with the complicatedness of the activity to which the deposit deposition of the SiC by law is carried out becomes small.

[0018] The carbonaceous crucible for single crystal raising of this invention is manufactured by the following method. First, the crucible Plastic solid which consists of C/C material is produced by fabricating by the method of applying immersion or matrix resin liquid to matrix resin liquid for carbon fiber textile fabrics with a conventional method in the crucible configuration of a request of the prepreg which sank in and carried out semi-hardening of the matrix resin to the carbon fiber, and carrying out the baking carbonization of the hardened Plastic solid all over the heating furnace held at the non-oxidizing atmosphere. In addition, as matrix resin, the thermosetting resin of high carbonization nature, such as phenol resin and furan resin, is used.

[0019] Or matrix resin liquid is sunk into a continuation carbon fiber, and after hardening the Plastic solid fabricated in the crucible configuration with the filament winding method, the crucible Plastic solid which consists of C/C material is also producible by carrying out baking carbonization all over the heating furnace held at the non-oxidizing atmosphere.

[0020] Thus, the carbonaceous crucible which consists of complex tissue of the C/C material and SiC with which SiC in which set the crucible Plastic solid which consists of produced C/C material in CVI equipment, and 35 - 50 vol% of the total pore capacity of this invention carried out the gaseous-phase deposit by processing by the specific CVI reaction condition, and which carried out deposition into pore was filled up is manufactured.

[0021] The CVI method (Chemical Vapor Infiltration) Unlike a CVD method (Chemical Vapor Deposition), gaseous-phase vacuum evaporation can be carried out to the micro front face in detailed pore or an opening. The CVI method is the technique, (a) soak and constant-pressure mold CVI, (b) forcible floating CVI, It is divided roughly into the (c) pulse CVI etc. among these, the pulse CVI -- that which enables law to be comparatively filled up with a sludge for a short time to the pore depths by carrying out evacuation of the ** system of reaction, and repeating the predetermined time maintenance for the gas removal in pore, flash installation of the material gas to ** system of reaction, and ** reaction deposit hundreds of thousands times from thousands as one pulse -- it is -- the object of this invention -- Pulse CVI -- law is applied preferably. However, it is not limited to the pulse CVI method.

[0022] The crucible Plastic solid which consists of C / C material is filled up with the inside of the pore of a crucible Plastic solid by carrying out gaseous-phase pyrolysis of the material gas which laid in the base material cradle of a CVI reactor, heated, and was supplied, and carrying out the deposit deposition of the SiC. the methyltrichlorosilane (CH_3SiCl_3) and methyl dichlorosilane ($\text{CH}_3\text{SiHCl}_2$) which contain Si atom and C atom in material gas in 1 molecule etc. -- the mixed gas of a halogenation organosilicon compound and hydrogen is used.

[0023] In order to make material gas permeate in pore by the CVI method, to carry out gaseous-phase pyrolysis and to carry out deposit restoration of the SiC into pore, setting-out control of the CVI reaction condition is carried out as follows.

** Carry out evacuation of the inside of the system of reaction, maintain under reduced pressure of 4 or less Torrs, and carry out blowdown clearance of the gas which exists in the pore of a C/C base material. If whenever [reduce pressure] exceeds 4Torr(s), the effect of degasifying will become inadequate, and since the blowdown clearance of the gas which exists in the depths in pore cannot fully be carried out, it becomes difficult to carry out deposit restoration of the SiC as a result even at the pore depths (evacuation process).

[0024] ** Introduce the mixed gas of a halogenation organosilicon compound and hydrogen momentarily as material gas, heating the inside of the system of reaction in temperature of 1100-1200 degrees C. In this case, the isolation frequency of amorphous Si becomes high into SiC which deposited that heating temperature was less than 1100 degrees C, and if it exceeds 1200 degrees C, it will become difficult to be filled up to the interior of pore, especially the pore depths. Furthermore, the concentration of the halogenation organosilicon compound in material gas is set as the range of 8 - 25 mol%. Since the heat transfer to material gas becomes it quick that the concentration of a halogenation organosilicon compound is under 8 mol% compared with diffusion of the material gas inside [of a C/C base material] pore, as a result of the deposit to a C/C base material front face having priority, SiC restoration inside pore becomes difficult. However, if concentration exceeds 25 mol%, as a result of the reaction frequency in a C/C base material front face becoming high as compared with material gas diffusion inside pore and the SiC deposit to a base material side having priority, SiC restoration inside [of C / C base

material] pore becomes difficult (material gas flash installation process). In this case, the maximum fill inside pore is less than [35 vol%].

[0025] ** Carry out deposit restoration of the SiC of the specified quantity inside pore by carrying out predetermined time maintenance at the CVI reaction condition set up by the above-mentioned ** (maintenance process).

[0026] The deposit deposition of the SiC can be carried out even to the pore depths of C / C base material by repeating hundreds of thousands times from thousands by making a series of processes of this ** evacuation process, ** material gas flash installation process, and ** maintenance process into one pulse, and it becomes possible to be filled up with the inside of with a total pore capacity [35 - 50 vol% of] pore. Thus, the interior of pore and the surface side of a C/C base material which constitute a carbonaceous crucible are filled up with and covered by SiC excellent in oxidation resistance by high intensity, reactivity with a quartz crucible falls also at the time of the heating at high temperature at the time of silicon single crystal raising, and generating of SiO gas and osmosis in the interior of pore of a C/C base material are inhibited effectively.

[0027] Hereafter, the example of this invention is concretely explained as contrasted with the example of a comparison.

[0028] The laminating of the prepreg sheet which applied the initial condensate of phenol resin, and air-dried [sank it in and] and created it to the 2-dimensional ** crossing of examples 1-3, the example 1 of a comparison - 5 polyacrylonitrile system carbon fiber was carried out, and it put into the mold, it heated in temperature of 250 degrees C, and the resinous principle was hardened. Subsequently, all over the heating furnace held on a nitrogen-gas-atmosphere mind, it heated at 2000 degrees C with the programming rate of 10 degrees C/hr, and it held for 5 hours and baking carbonization was carried out. Thus, the test piece which consists of a 25x25x4mm C/C base material (Vf: about 60%) was produced.

[0029] This test piece was set in the reactor of outside heat type horizontal-type pulse CVI equipment, evacuation of the inside of a system was carried out, and the inside of a furnace was decompressed to 3 - 4Torr. Subsequently after heating and reaching predetermined temperature, by making the mixed gas of TORIKURORO methylsilane (CH₃SiCl₃) and hydrogen into material gas, it introduced in the furnace, predetermined carried out the time amount reaction, and it was deposited and filled up with SiC in the pore of a test piece by the CVI reaction. the weight rate of increase perform a repeat CVI reaction for a series of actuation of this evacuation process, material gas flash installation process, and maintenance process ** as one pulse, and according to the deposit of SiC, and restoration -- 25wt(s)% -- it carried out repeatedly until it became order. Under the present circumstances, CVI reaction conditions, such as reaction temperature, TORIKURORO methylsilane concentration in material gas, and a count of a pulse, were changed. In addition, the other CVI reaction conditions are as follows.

evacuation process: -- purge timing; -- 1.9-second material gas installation process; *****; -- 200Torr, and installation time; 0.7-second maintenance process; holding-time; 1.0-second one pulse; 3.6 seconds [0030] Thus, the CVI reaction condition which deposited and filled up the test piece with SiC was shown in a table 1 by comparison.

[0031]

[A table 1]

例No.	反応温度 (℃)	原料濃度 (mol %) *1	パルス回数
実施例 1	1 2 0 0	1 2 . 6	2 0 0 0
実施例 2	1 1 0 0	1 0 . 0	4 0 0 0
実施例 3	1 2 0 0	1 9 . 5	2 0 0 0
比較例 1	9 0 0	1 0 . 0	1 6 0 0 0
比較例 2	1 0 0 0	1 0 . 5	9 0 0 0
比較例 3	1 2 0 0	1 . 0	2 0 0 0 0
比較例 4	1 2 0 0	2 6 . 3	2 0 0 0
比較例 5	1 3 0 0	1 0 . 2	3 0 0 0

(Note) *1 Concentration of the TORIKURORO methylsilane in the material gas which mixed TORIKURORO methylsilane (CH₃SiCl₃) and hydrogen [0032] The test piece was immersed into the solution which dissolved

c b e e e f c e e f h e g h f c c e f e h g

drying polycarbosilane and removing a xylene, it heated in temperature of 250 degrees C among atmospheric air for 5 hours, and non-deliquesce processing was carried out. After repeating this processing 3 times, it heated in temperature of 1500 degrees C in nitrogen-gas-atmosphere mind, polycarbosilane was pyrolyzed, and the SiC coat was formed in the test piece.

[0033] Next, about the test piece which deposited and was filled up with these SiC(s), the weight rate of increase, surface thickness, a filling factor, surface membrane quality, etc. were measured by the following method, and the oxidation-resistant trial was performed. The obtained result was shown in a table 2.

[0034] (1) Weight rate of increase; the weight variation of the test piece before and behind a reaction was measured with the electronic balance, and weight variation was ΔW and computed by the weight of the test piece before reacting.

(2) Surface thickness; the test piece after a reaction was cut, the cutting plane was observed with the scanning electron microscope, and thickness was measured and averaged.

(3) filling factor; -- volume increment ΔV after a reaction (delta w/rho) from -- the surface deposit volume V_s of a test piece (V_0) the internal deposit volume reduced and obtained -- (pore volume V_p) cm^3/g of a test piece It computed from the degree type by making into a filling factor the rate of occupying.

filling factor (vol%) = $[(\Delta V / \rho) - (V_0)] / (W_0 \cdot V_p) \times 100$ however ΔV ; weight augend, the sludge thickness on the front face of a test piece measured from h; scanning electron microscope photograph, and W_0 ; The weight of a test piece, and V_0 ; The density (3.10 g/cm^3) of surface area ρ ; SiC of a test piece, and V_p ; $0.1452 \text{ (cm}^3/\text{g)}$ it is .

(4) Surface membrane quality; the X diffraction estimated the crystal reinforcement on the front face of a test piece.

(5) An oxidation-resistant trial; it put into the electric furnace of an atmospheric-air ambient atmosphere, and heated, and after holding for 30 minutes in temperature of 500 degrees C, it cooled naturally from a furnace to ejection ordinary temperature. Next, after heating in temperature of 600 degrees C and holding for 30 minutes, it cooled naturally from a furnace to ejection ordinary temperature. Thus, heated actuation which carries out temperature up 100 degrees C at a time was performed to 1000 degrees C, the weight percentage reduction at that time was computed from the following type, and oxidation resistance was evaluated.

Weight percentage reduction (%) = $(W_0 - W_{1000}) / (W_0) \times 100$, however W_0 W_{1000} is the weight of the test piece before an anti-oxidation trial, and the weight of the test piece after performing a heat test to 1000 degrees C. [0035

[A table 2]

例No.	重量増加率 (wt%)	表面膜厚 (μm)	充填率 (vol%)	表面膜質	重量減少率 (wt%)
実施例 1	26.0	35	45	β -SiC	13.5
実施例 2	27.4	35	46	β -SiC	16.1
実施例 3	26.3	56	37	β -SiC	16.7
比較例 1	24.0	26	44	非晶質Si	14.6
比較例 2	26.8	34	47	非晶質Si	15.3
比較例 3	23.3	88	20	β -SiC	19.3
比較例 4	25.3	94	24	β -SiC	18.7
比較例 5	22.7	126	9	β -SiC	21.4
比較例 6	25.9	108	20	β -SiC	19.2

[0036] It is admitted that 35 - 50vol % of pore capacity is filled up with the example from the result of tables 1 and 2 by SiC which deposited by the CVI method, and the weight percentage reduction by oxidation treatment is in lower order. On the other hand, although the examples 1 and 2 of a comparison also show oxidation resistance equivalent to examples 1-3, since the film formed in the front face is amorphous Si, it is converted into SiO_2 by oxidation treatment, causes buildup of weight, and is judged to be what has weight percentage reduction in lower order seemingly. Furthermore, since CVI temperature is low, it is necessary to increase the count of a pulse substantially, and it becomes inefficient. In the example 3 of a comparison, it turns out that the filling factor of SiC

is low even if it makes [many] the count of a pulse, since raw material concentration is low, and the percentage reduction by the oxidation test is large. In the example 4 of a comparison, since raw material concentration is high the thickness in a base material side is thick, and a crack occurs, and since the filling factor of SiC is moreover also low, it turns out that the percentage reduction by the oxidation test is large. Moreover, in the example 5 of a comparison, since CVI temperature is high, thickness in a front face can be thickened, but a crack occurs, and since the filling factor of SiC is moreover also low, it turns out that the percentage reduction by the oxidation test is large.

[0037]

[Effect of the Invention] As above, the carbonaceous crucible for single crystal raising of this invention Since it consists of complex of the C/C material filled up with SiC which deposited by law, and SiC, reactivity with a quartz crucible is low. 35 - 50 vol% of the total pore capacity of a C/C base material -- CVI -- Since generating of SiO is inhibited effectively, SiC-ization of the carbonaceous crucible by SiO gas is controlled, an activity life is long and the carbonaceous crucible excellent in endurance is offered. Moreover, according to the manufacture method, it becomes possible by specifying a CVI reaction condition to manufacture the carbonaceous crucible excellent in endurance easily.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] carbon fiber consolidation carbon material -- a base material -- carrying out -- 35 - 50 vol% of total pore capacity of this base material -- CVI -- a carbonaceous crucible for single crystal raising characterized by consisting of complex of carbon fiber consolidation carbon material filled up with SiC which deposited by law, and SiC.

[Claim 2] Use carbon fiber consolidation carbon material obtained by carbon fiber by carrying out matrix resin at impregnation and carrying out the baking carbonization of the hardened crucible Plastic solid under a non-oxidizing atmosphere as a base material, and this base material is set in CVI equipment. A process which sets concentration of a halogenation organosilicon compound in material gas as 8 - 25 mol%, and carries out flash installation by making mixed gas of a halogenation organosilicon compound and hydrogen into material gas while heating the inside of a system to a process and temperature of 1100-1200 degrees C which carry out evacuation to a pressure of 4 or less Torrs, A manufacture method of a carbonaceous crucible for single crystal raising according to claim 1 characterized by carrying out deposit restoration of the SiC for a series of actuation which consists of a process which carries out predetermined time maintenance in order to pyrolyze material gas by the CVI reaction and to deposit SiC into a repeat deed and pore of a base material as one pulse.

[Translation done.]